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COLLOIDAL ASSEMBLIES EFFECT ON CHEMICAL REACTIONS(U)
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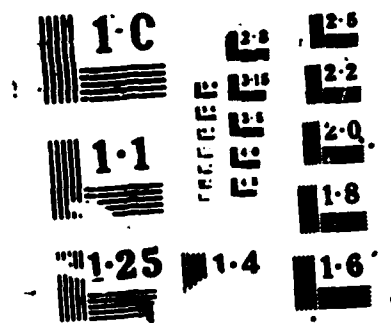
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COLLOIDAL ASSEMBLIES EFFECT ON CHEMICAL REACTIONS

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PROGRESS OF THE RESEARCH

Photocatalytic Degradation of Organic Compounds

The photoassisted reactions on semiconductor materials for the degradation of hazardous organic compounds have been applied to sparingly soluble halogenated aromatic compounds (e.g. Dioxins, PCB, DDT).^{1,2} Complete disappearance of the initial compounds and stoichiometric formation of chloride after irradiation in the presence of TiO_2 have demonstrated the efficiency of the process even for these environmentally long-living compounds.

Among the herbicides, the class of s-triazine pesticides is under investigation. The kinetics and the identification of the intermediates have been carried out.³

An exhaustive review on the application of the photocatalytic processes to the environmental control and to the disposal of hazardous wastes has been presented before a recent NATO ASI and will soon appear in a book.⁴

Effect of Solvent Composition on Oxidation Reactions

The effect of solvent composition (alcohol/water; DMF/water; DMSO/water) on the oxidation kinetics of benzenediols by means of hexachloroiridate(IV) has been investigated. The interpretation of the solvent effect is based on the initial state/transition state analysis.⁵ Relevant effect of the solvent composition on the reaction rates (up to more than three orders of magnitude) has been observed.

Reactivity in Micellar Aggregates

The kinetics and mechanism of complex formation between iron(III) and 4-alkylamido-2-hydroxybenzoic acids (with different alkyl chain) has been investigated in the presence of non-ionic surfactant. The partitioning of the reagents and products and the effect of the aggregates on the rates have been interpreted in the light of a pseudo-phase model.⁶

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The electron transfer equilibria of a series of N-alkyl-phenothiazine (alkyl = methyl, ethyl, n-butyl) with iron(III)/(II) has been investigated in the presence of anionic, cationic and non-ionic surfactant aggregates. The effect of the micelles on the equilibria quotients and reaction rates has been analyzed in terms of interactions of reagents and products with the organized assemblies. The contribution of the electrostatic interactions and of the N-alkyl chain hydrophobicity has been evidenced.

Reactivity in Microemulsions

The electron transfer rate of reaction between two highly hydrophilic ions, e.g. IrCl_6^{2-} and $\text{CoW}_{12}\text{O}_{40}^{0-}$, has been investigated over a wide range of composition in a SDS/1-butanol/toluene/water-0.09 M NaCl - 0.01 M HCl microemulsion. In the light of our previously reported three-phase-model (Langmuir, 1988, 4, 101), informations on the "free" water in the droplets, the upper demixing line and the structured regions of the microemulsion have been obtained.

Other microemulsion systems obtained with different oil phase have been considered. Suggestions on the effect of the nature of the oil on the "structure" of the microemulsions in different zones have been proposed.

Physico-chemical Properties of Surfactant Aggregates

The properties of aggregates obtained from "functionalized" surfactants; in particular bearing polar heads having complexing capability, are actually under investigation.

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- 8 - C.Minero, E.pramauro, and E.Pelizzetti, submitted.
- 9 - C.Minero and E.Pelizzetti, in progress.
- 10 - E.Pramauro and E.Pelizzetti, in progress.

2 Research Plans

- Photodegradation of organic compounds by visible light.

Other organic compounds of environmental interest will be examined. The investigation of the details of the reaction mechanism, i.e. adsorption-desorption process, kinetics, intermediate detection, will be pursued. Attention to the optimization of the catalyst and to other materials (including immobilization of the catalyst) will be deserved.

- Reactivity in organized assemblies.

The effect of aggregates, such as micelles and microemulsions, on the electron transfer reactions as well as on complex formation reaction will be explored with particular attention to catalytic process. The properties of aggregates with reactive components will be investigated.

- The effect of solvent composition on oxidation reactions.

The effect of organic solvent/water mixtures on electron transfer reactions involving sparingly soluble (in water) compounds will be considered.

- Physico-chemical properties of aggregates.

These properties will be investigated with particular attention to aggregates originated from "functionalized" surfactants.

- 3 No significative administrative actions occurred during the period reported.

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- 6 The funds of the fifth instalment are now available.

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